

The Exchange of Energy Between Organic Molecules in a Molecular Beam and Metallic Surfaces

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
HAROLD THEODORE BYCK
Baltimore, 1930

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THE EXCHANGE OF ENERGY BETWEEN ORGANIC
MOLECULES IN A MOLECULAR BEAM AND
METALLIC SURFACES.

BY

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AND

HAROLD T. BYCK, PH.D.

The Exchange of Energy between Organic Molecules in a Molecular Beam and Metallic Surfaces.

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When a molecular beam of a substance is directed against a heated target, the molecules rebound and, together with any fragments resulting from decomposition, can be caught on a liquid air-cooled surface. Since the fragments are in a molecular beam they cannot react before reaching the liquid air surface and we may expect, therefore, that work of this kind will yield considerable information about the nature of the primary change in chemical reactions.

Furthermore, we may expect to obtain information about the exchange of energy between solid surfaces and gaseous molecules. Experiments on the heat conductivity of gases at low pressure have yielded considerable information on this exchange of energy and there has been a number of papers dealing with the theoretical aspects of the problem.* We must here emphasise the important point that in practically all previous work, both theoretical and experimental, only small molecules have been considered; in these cases the internal energy

* Baule, 'Ann. Physik,' vol. 44, p. 145 (1914); further references are included in two recent papers, Roberts, 'Proc. Roy. Soc.,' A, vol. 129, p. 146 (1930); Johnson, *ibid.*, vol. 128, p. 432, p. 444 (1930).

has been completely neglected and only the kinetic energy of the molecules has been considered. It is obvious that when we are dealing with the chemical decomposition of large molecules, any changes in kinetic energy after collision with the wall must be relatively unimportant compared with changes of internal energy; therefore, we shall consider only the transfer of energy from the wall to the internal degrees of freedom.

It has been supposed that when a beam of molecules collides with a surface, a certain fraction is adsorbed or enters the space lattice for a time which is long compared to the duration of a collision. If we assume that an appreciable fraction of the organic molecules remains in contact with the surface for a long time compared to the duration of a collision, we should observe decomposition at temperatures as low as 600° C., since the organic molecules used decompose readily at this temperature. In our experiments with a platinum target, we found no decomposition at any temperature up to 1600° C., either with acetone or dimethyl mercury, and it seems unlikely, therefore, that adsorption plays any important rôle in collisions of these molecules with a heated platinum surface.

Apparatus and Experimental Procedure.

The first step in carrying out a run was the evacuation and outgassing of the entire system, a diagram of which is given in fig. 1. The acetone reservoir (R), fig. 1, was surrounded with liquid air and opened through stopcock (Y) to the apparatus. The levelling bulbs for traps (T_1) and (T_2) were lowered so that the oil pump was connected through (P_2) to the Toepler pump (B) and to the Gaede diffusion pump (D_2), and through (P_1) to the glass diffusion pump (D_1). When the system had been evacuated to the limit of the oil pump, both diffusion pumps were started and pumping continued for several hours. By alternately freezing and melting the acetone in its reservoir, meanwhile continuing the pumping, all dissolved gases were removed, and in later runs it was unnecessary to repeat this portion of the evacuation. The stopcock (Y) closing off the reservoir from the system was then closed.

The Jet.—The beam of molecules was formed by aiming a small jet, through which the acetone was admitted, directly at the heated metal target. The jet used in all of these experiments was of quartz tubing pulled down to small diameter with an opening 0.4 mm. in diameter. The external diameter of the jet was made small in order that it offer little obstruction to molecules flying from the target toward the condensing surface.

The quantity of acetone flowing through the jet on to the target was deter-

mined by calibration. The substance was contained in a small glass reservoir connected to the jet. The pressure at the mouth of the jet within the apparatus

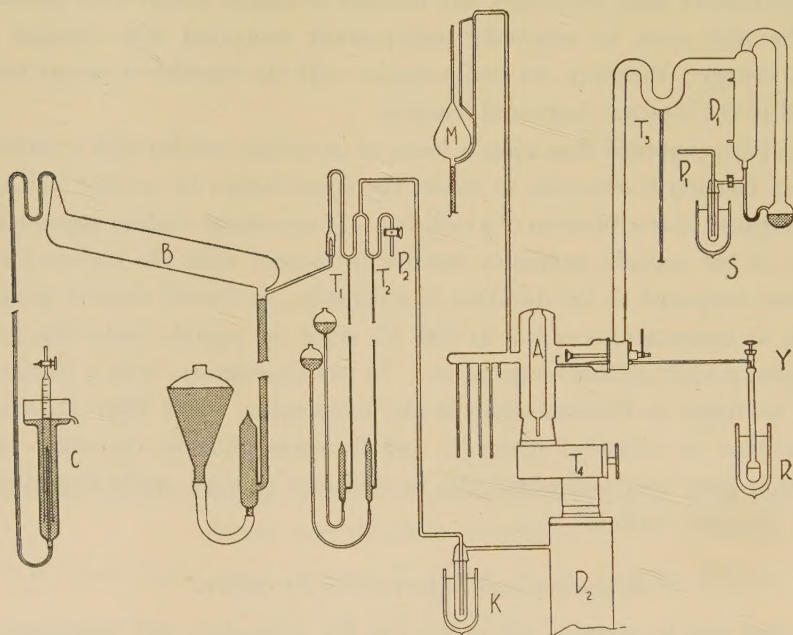


FIG. 1.

was kept below 10^{-5} mm. Hg, and by varying the temperature of the reservoir the vapour pressure of the acetone could be fixed at a value to give any desired rate of flow through the jet into the apparatus.

Calibration was accomplished by maintaining the acetone in the reservoir at some constant temperature (for example, -32° C. with liquid ammonia). Then, after evacuating the system to 10^{-5} mm. and filling the condensing trap with liquid air, the stopcock between the reservoir and the jet was opened. The acetone under the difference in pressure between its vapour pressure at -32° in the reservoir, and 10^{-5} mm. at the mouth of the jet, flowed through the jet on to the target (which was not heated during calibration runs) from which it rebounded on to the liquid air surface, and was condensed.

The calibration was carried on for 2 hours, after which the reservoir was closed off from the jet and the condensed acetone was distilled into a side tube which was sealed off and the weight of acetone determined; as an additional check the acetone was determined by Messinger's method.* From these

* Goodwin, 'J. Amer. Chem. Soc.,' vol. 42, p. 39 (1920).

figures, the rate of flow of acetone, in milligrams per hour, for different reservoir temperatures was calculated.

The beam of molecules spread out fanwise from the jet, and since the rectangular foil did not cover the entire cross section of the circular tube, some of the acetone missed the target and passed behind it. A two-stage glass diffusion pump was connected behind the foil to remove this acetone, in order to prevent its building up a pressure in that space. This acetone was pumped to waste, and was not included in the calibration value, since it was assumed that this same quantity was lost during different runs.

The Target and Supports.—The target against which the molecular beam impinges was of metal in the form of foil 21 mm. $\times$ 25 mm. and 0.025 mm. thick. It was supported by two tantalum stirrups, to which it was clamped along opposite edges by small bars of the same metal screwed against the stirrups proper. The stirrups in turn were fixed into slots in the ends of the copper electrodes and were clamped by small brass collars (see fig. 2).

The electrodes were of pure copper, $\frac{3}{8}$ inch in diameter sealed through a steel shell with red sealing wax. The steel shell, carrying the electrodes and jet, and a tube leading to the waste pump, was sealed against the glass side-tube with red sealing wax also. Each electrode was insulated from the steel shell by a thin pyrex bushing. The electrodes were drilled out to within $\frac{1}{16}$ -inch of the slotted inner ends, and a brass bushing at the outer end supported a small glass tube extending the length of this hole. Each electrode where it was sealed through the steel shell was fitted with a water-cooled jacket to prevent the seals from becoming soft. The cooling water circulated within these jackets entered the hollow portion of the electrodes, flowed their length to the end supporting the foil, and left through the glass tube mentioned above. This water-cooling system was adequate to maintain all the metal parts of the supporting system at room temperature, and no difficulty was experienced in keeping the wax hard and vacuum tight.

The resistances of the various metal foils used were of the order of 0.02 ohms and to raise them to high temperatures it was necessary to use heavy currents. A step-down transformer operated from the 120-volt A.C. line gave 60 to 130 amp. at 12 volts.

Temperature Measurement.—The temperature of the foil was measured with a Leeds and Northup optical pyrometer, of the type whose operation depends on matching the brightness of a standard tungsten filament with the brightness of the unknown source filtered through certain red filters which pass a narrow spectral region at about 6500 Å. The instrument used was

previously calibrated by the Bureau of Standards. In making readings, the telescope was pointed at the foil as nearly perpendicularly as the configuration

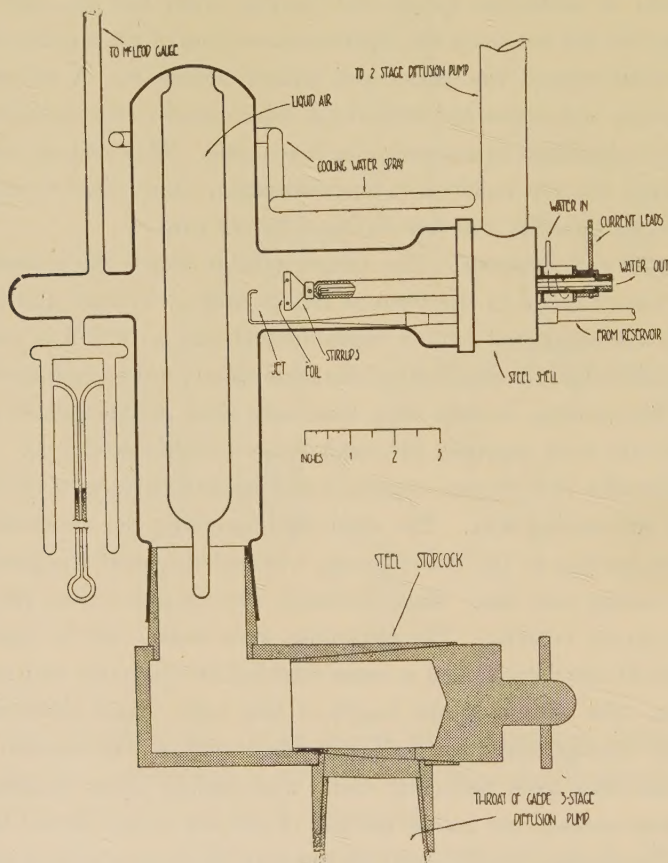


FIG. 2.

of the apparatus would permit, and the current to the standard tungsten filament was regulated until the filament faded into the background of light from the hot foil. This reading in milliamperes was then converted to temperature and a correction made for the brightness temperature of the metal in use during any particular experiment. The values for the brightness correction are taken from vol. 5 of the 'International Critical Tables,' p. 245. This correction is about 150°C . for all three metals used (Ta, W, Pt) in the region 1600° to 1700° , the actual temperature being higher by that amount than the temperature measured on the pyrometer.

Pumps.—After the organic molecules had left the jet and collided with the

heated metal target, the products rebounded to the liquid air-cooled surface (A), where acetone or other condensible material was caught and the uncondensed gaseous products of the reaction were removed by the Gaede steel pump (D_2). This pump was capable of operating against a fore-pressure of 20 mm., but we never allowed this to rise above 1 mm. to insure that the pump continued to operate at high efficiency, since the pressure in the decomposition chamber was kept below 6×10^{-5} mm. During the run the uncondensed gaseous products passed from the steel diffusion pump to the Toepler pump (B) in which they could be compressed from the low pressure prevailing at the outlet of the diffusion pump, to atmospheric pressure and collected over mercury. The Toepler pump was emptied at frequent intervals since it acted as the forepump to the Gaede pump; even for large evolutions of gas, 5-minute pumping intervals were sufficient to keep the fore-pressure below a millimetre.

Experimental Procedure in Detail.—After the system was evacuated the foil was heated slightly higher than the temperature to be used in the run and pumping continued for several hours more. Trap (T_2) was raised, cutting off the oil pump and connecting the Toepler pump directly to the fore-pump side of the Gaede diffusion pump. The Toepler pump was emptied at 15-minute intervals and the small volume of gas coming from the hot foil and from the walls of the apparatus was collected in the burette (C). It was found that the volume of gas coming off per half-hour after several hours' pumping was too small to be measured in the burette. Out-gassing was considered complete after about 2 hours' evacuation with the foil heated, and after an additional hour of pumping the run was started.

In the meantime the acetone reservoir (R) had been surrounded with a cooling bath contained in a Dewar flask. The substance used for this bath was previously determined by calibration of the jet. The temperature of this bath was measured with a pentane thermometer during the run and remained constant to 0.2° . Traps (K) and (S) were now immersed in liquid air, and liquid air run into the trap (A) in the decomposition chamber.

The run was started by opening the stopcock (Y) between reservoir and jet. The Toepler pump was emptied at 5-minute intervals and the gas evolved measured after each pumping. The pressure within the decomposition chamber was measured on the McLeod gauge (M) at 15-minute intervals, and the temperature of the foil read with the optical pyrometer at similar time intervals. It was necessary to add liquid air to the trap in the decomposition chamber at 3 to 4-minute intervals while the foil was lit. Although heat conduction from the foil to the cold surface was practically zero at the low pressure prevailing,

a film of condensed mercury from the diffusion pumps formed a dark grey deposit which absorbed considerable infra-red radiation from the foil, and rapid evaporation of the liquid air took place.

At the end of the run, the foil current was turned off, the acetone reservoir closed off from the jet, and pumping with the Toepler pump was continued for several more 5-minute periods to insure removal of all the gases resulting from decomposition. It was found that two such pumpings at 5-minute intervals were sufficient to remove the last small volume of gas, subsequent pumpings producing samples of gas too small to be measured.

The decomposition chamber was next isolated from the rest of the apparatus by raising mercury in trap (T_3) to cut off the glass diffusion pump, raising the mercury in the McLeod gauge (M) above the inlet to close it off, and finally closing the large steel stopcock (T_4) to cut off the Gaede diffusion pump. A Dewar flask containing liquid air was slipped up over one of the sample tubes (L) sealed into the side arm of the decomposition chamber, the liquid air pumped out of the trap in the chamber, and the condensed products distilled into this side tube. This was then sealed off and contained the condensible products of decomposition from the run.

In some of the runs this collecting tube had the form of a quartz absorption cell and, after sealing off, ultra-violet absorption spectra were made.

The small tube containing the condensed products was weighed, and, after the sample was removed, weighed again, the difference giving the weight of the recovered material.

In several runs this material was condensed directly into an apparatus for determining its mean molecular weight by the vapour density method. In still other runs the sample tube formed one arm of a manometer, the other arm containing pure acetone. By thermostating the whole manometer after it was sealed off, the difference in vapour pressure between pure acetone and the unknown material was measured.

The foil was removed from its supports and weighed after the run, any difference between this weight and its original weight being noted.

In those experiments where the foil was not removed, the long outgassing period was not repeated since the vacuum had not been broken. The run in such cases was started after heating the target for several hours with the pressure at 10^{-5} mm. or better.

The gas sample collected in (C) was removed and analysed in a standard gas analysis apparatus for CO_2 , unsaturated hydrocarbons, O_2 , H_2 , CO , and saturated hydrocarbons.

Experimental Results.

Low Temperature Experiments.—We shall present first the low temperature experiments with tantalum and tungsten which show complete absence of decomposition below 1000° C. In Table I we give the details of the runs made with acetone on tungsten.

Table I.—Acetone on Tungsten (850°, 940°, 1085° C.). The Gas Evolved was Measured at 5-minute Intervals.

Foil temperature.	Time.	Gas evolved per hour.
° C.	minutes	c.c.
850	30	0·0
940	60	0·0
1085	30	0·6

A similar series of runs at 700°, 800°, 900° and 1400° C., using tantalum instead of tungsten, gave no decomposition and it was not until 1500° was reached that we observed decomposition on a tantalum surface.

Acetone on Tantalum.—The complete experimental details will now be given for one run in which decomposition was obtained. We have selected a typical experiment in which acetone was decomposed on a new tantalum foil in the neighbourhood of 1600° C. and the rate of gas evolution and the results of the gas analysis is given in Tables II and III. It will be seen from the results

Table II.—Acetone on Tantalum. New Foil 1600° C. The Gas Evolved was Measured at 5-minute Intervals.

Foil temperature.	Time	Total gas evolved.	Average hourly rate.
° C.	minutes		
1580	30	5·10	10·20
1580	60	9·40	8·60
1580	90	13·50	8·20
1580	120	17·50	8·00
1590	150	21·40	7·80
1590	180	24·90	7·00
1600	210	29·20	8·60
1600	300	31·00	7·20

Near the end of this run, owing to the Toepler pump going out of order, the gaseous products were sent to waste for 75 minutes. Because of this, the total amount of gas given off during the run was not 31·00 cc. but 300/225 of 31·0 cc.

shown in Table II that the rate of evolution of gas shows a small but steady diminution over each hourly period. The gas analysis showed the presence of carbon monoxide and hydrogen only; there was no trace of methane or other saturated hydrocarbons since after combustion with oxygen no carbon dioxide was found.

Table III.—Acetone on Tantalum at 1600° C. Analysis of Permanent Gases Evolved.

Sample of gas (at 28·0° C.)	31·2 c.c.
Absorption in KOH.....	0·3 c.c. CO ₂ .
Absorption in fuming H ₂ SO ₄	0·0 c.c. unsaturated.
Absorption for oxygen	0·6 c.c. oxygen.
Absorption for CO	7·5 c.c. CO.
Combustion for H ₂	18·7 c.c. hydrogen.
Absorption in KOH (saturated hydrocarbons)	0·0 c.c.
Residual nitrogen.....	3·0 c.c. nitrogen.

It will be observed that we have collected 7·5 c.c. CO and 18·7 c.c. H₂ which represent substantially all of the permanent gases produced in the decomposition. This gives a mole ratio of H₂/CO = 2·5/1 which represents the average ratio of the gases produced over the period of the run. The total amount of CO and H₂ evolved during the run was 9·99 c.c. and 24·9 c.c. respectively since the amount collected must be multiplied by the factor mentioned in Table II. If we assume that each molecule of CO produced corresponds to each molecule of acetone decomposed, we can calculate the weight of acetone decomposed, which is 0·0235 grms. corresponding to 9·99 c.c. of CO. The weight of acetone recovered undecomposed was 0·1167 grms., so that 16·7 per cent. of the acetone was decomposed.

We had previously calibrated the jet delivering the acetone, so that we knew the total amount of acetone which should have entered the system. This was 0·3425 grms. for the entire run, which is in entire disagreement with the value $0·1167 + 0·0235 = 0·1402$ grms. based on the weight recovered and the CO obtained. We attribute this to the fact that the calibration was necessarily made with the foil cold; during the run with the foil at 1600° C. the small diameter tube from which the acetone issued as a beam must have become heated perhaps to 200–300° C. by radiation; the increased viscosity of the gaseous acetone is presumably responsible for the much smaller amount of acetone recovered.

Table IV.—Acetone on Tantalum. Old Foil. 1700° C. The Gas Evolved was Measured at 5-minute Intervals.

Foil temperature.	Time	Total gas evolved.	Average hourly rate.
° C.	minutes		
1700	30	4.90	9.80
1700	60	8.60	7.40
1710	90	11.70	6.20
1710	120	13.90	4.40
1710	150	15.40	3.00
1710	180	16.90	3.00
1670	210	18.30	2.80
1640	240	19.50	2.40
1640	300	21.80	2.30

We shall now give the results of a second run at a higher temperature in which we used the same tantalum foil as before. It will be seen that there is a considerable fall in the rate of evolution of gas, the rate in the last part of the run being much less than previous run at 1600° C. In Table V we give the results of the gas analysis; the ratio of $H_2/CO = 2.2/1$ is substantially the same as in the previous run. The amount of acetone decomposed based on the CO recovered was 0.0148 grms. and the weight of acetone recovered undecomposed was 0.1179 grms. which corresponds to 11.1 per cent. decomposition. The efficiency of the foil in decomposing acetone therefore diminishes very greatly as the foil is used; we made several other runs with other tantalum foils over this range of temperature and observed this same behaviour in all cases.

Table V.—Acetone on Tantalum at 1700° C. Analysis of Permanent Gases.

Sample of gas (at 28.0° C.)	21.1 c.c.
Absorption in KOH.....	0.0 c.c. CO_2 .
Absorption in fuming H_2SO_4	0.0 c.c.
Absorption for oxygen	0.3 c.c. O_2 .
Absorption for CO	6.3 c.c. CO .
Combustion for H_2	13.8 c. c. H_2 .
Absorption in KOH (saturated hydrocarbons)	0.0 c.c.
Residual nitrogen.....	1.5 c.c. H_2 .

We have given an analysis of the permanent gases but we have not as yet given the details of the examination of the undecomposed acetone and other possible products condensed on the liquid air surface, which at the end of a run were evaporated into a small side arm and weighed.

A number of qualitative tests were made on samples from various runs.

The liquid in all cases had a characteristic and persistent odour resembling, perhaps, higher unsaturated hydrocarbons; however, treatment with bromine or potassium permanganate showed practically no unsaturated material. Special tests showed the absence of acetylene or allylene, and the absorption spectrum of the material showed the absence of benzene or other aromatic hydrocarbons. Furthermore, in one experiment in which considerable decomposition occurred the acetone was estimated by Messinger's method, which gave 0.1463 grms. acetone, whereas the weight of the sample was 0.1440 grms. In two other experiments we made a molecular weight determination of the sample and obtained the values 59.5 and 55.0; since we had only about 0.1 gm. with which to make the determinations, the experimental error is large and the figures are in satisfactory agreement with the theoretical value of 58 for pure acetone. There is undoubtedly formation of some condensible material which is caught with the acetone on the liquid air surface and which we have not been able to identify, but we feel that it is formed in such small quantity that we may safely disregard it.

We have now to give the experimental evidence that the reaction consists of a molecule of acetone decomposing at the surface with evolution of one molecule of CO and three molecules of H_2 , the two remaining carbon atoms combining with the tantalum. On the basis of this hypothesis we would expect the measured H_2/CO ratio to be 3.0, whereas the value obtained varied from 2.2 to 2.7. We have not been able to find the cause of this discrepancy but suggest two possibilities, namely diffusion through the foil of hydrogen, which would then be lost through the waste pump, or loss of hydrogen through formation of small quantities of higher hydrocarbons which would be caught with the acetone on the liquid air surface.

As an experiment progressed the original silver colour of the foil changed to gold and this colour extended right through the foil, which became very brittle and had a higher electrical resistance. After the two experiments just described were completed, we removed and weighed the foil and found an increase of 0.0170 grms.; the weight of acetone decomposed in these two runs was 0.0383 grms. and two-thirds of the carbon contained in this weight is 0.0168 grms., which is very near the increase in weight of the foil. An experiment to determine whether the carbon was in the free state was made by boiling the pieces of the foil in concentrated nitric acid which caused no change whatsoever in the colour of the foil; therefore the carbon could not be present as a free surface film.

Acetone on Tungsten.—The results with tungsten were similar to those

obtained with tantalum except that decomposition occurred at a lower temperature. We gave the results of a typical experiment in Tables VI and VII. Due to carbide formation the resistance of the tungsten foil increased considerably during the run and this partly accounts for the wide fluctuations in temperature. As with tantalum, the permanent gases consisted of CO and H₂ and showed no CO₂ after combustion, thus proving the absence of methane or other saturated hydrocarbons. The H₂/CO ratio is 2.56/1 which is similar to the value obtained for tantalum. The amount of acetone decomposed based on the CO recovered was 0.0189 grms. and the weight of acetone recovered undecomposed was 0.1451 grms. which corresponds to 11.5 per cent. decomposition. At the end of the run the tungsten foil was removed and weighed and gave increase in weight of 0.0067 grms., whereas the calculated increase of two-thirds of the carbon in the decomposed acetone is 0.0081 grms., which is within experimental error the same.

Table VI.—Acetone on Tungsten at 1650–1870° C. The Gas Evolved was Measured at 5-minute Intervals.

Foil temperature.	Time	Total gas evolved.	Average hourly rate.
° C.	minutes		
1650	30	5.00	10.00
1650–1750	60	10.90	11.80
1750–1870	90	17.00	12.20
1870	120	21.90	9.80
1870–1810	150	26.70	9.60
1810	180	29.20	5.00

Table VII.—Acetone on Tungsten at 1650–1870° C. Analysis of Permanent Gases Evolved.

Sample from run (at 28.5° C.)	30.20 c.c.
Absorption in KOH.....	0.10 c.c. CO ₂ .
Absorption in fuming H ₂ SO ₄	0.00 c.c. unsaturated.
Absorption for oxygen	0.20 c.c. O ₂ .
Absorption for CO	8.05 c.c. CO.
Combustion for H ₂	20.64 c.c. H ₂ .
Absorption of CO ₂ from combustion	0.0 c.c.
Residual nitrogen	0.90 c.c. nitrogen.

Dimethyl Mercury on Tantalum.—We have one experiment in which we used dimethyl mercury on a tantalum target and obtained the results given in Tables VIII and IX. The decomposition process is therefore very similar

to that with acetone, since the two carbon atoms combine with the tantalum and free hydrogen is liberated. Assuming that all the hydrogen from the decomposed dimethyl mercury is recovered in the pump we obtain a value 0.0464 grms. decomposed, whereas the weight recovered was 0.1161 grms., which corresponds to 28.5 per cent. decomposed. In this experiment as in the previous ones the foil turned golden and became very brittle. It increased in weight by 0.0060 grms., whereas the carbon in the decomposed dimethyl mercury weighed 0.0048 grms.

Table VIII.—Dimethyl Mercury on Tantalum. New Foil (1680–1740° C.).
The Gas Evolved was Measured at 5-minute Intervals.

Foil temperature.	Time	Total gas evolved.	Average hourly rate.
° C.	minutes		
1680	30	3.20	6.40
1680	60	5.50	4.60
1680	90	7.40	3.80
1680–1720	120	9.20	3.60
1720	150	10.85	3.30
1720	180	12.35	3.00
1720	240	15.10	—
1740	300	17.60	—

Table IX.—Dimethyl Mercury on Tantalum. Analysis of Permanent Gases.

Sample from run (at 23.5° C.)	16.50 c.c.
Absorption in KOH.....	0.0 c.c. CO.
Absorption in fuming H ₂ SO ₄	0.0 c.c. unsaturated.
Absorption for oxygen	0.2 c.c. O ₂ .
Absorption for CO	0.4 c.c. CO.
Combustion for H ₂	14.7 c.c. H ₂ .
Absorption in KOH (saturated hydrocarbons)	0.0 c.c. saturated.
Residual nitrogen.....	0.8 c.c. N ₂ .

Acetone on Platinum.—We made one run lasting 120 minutes using a platinum target at 1600° C., and obtained no decomposition whatsoever. At the end of the run the whole apparatus near the target was coated with platinum which had distilled from the foil during the experiment. We recovered 0.0374 grms. of acetone, which had the usual sweet odour and was quite free from the characteristic odour obtained in the previous runs.

When calibrating the system for the amount of acetone entering we found that under our conditions with the foil cold 0.1370 grms. were obtained in 2 hours. The heating effect by radiation on the narrow tube through which the

acetone passes must be considerable and in this experiment was augmented by the platinum black deposited on it.

Dimethyl Mercury on Platinum.—A run of 90 minutes was made on a platinum target at 1600° C., but again we obtained no decomposition. The amount of dimethyl mercury recovered was 0.0359 grms., whereas based on a calibration with the target cold we should expect to obtain 0.1500 grms.

Discussion of Results.

We shall first consider the results obtained, using the platinum target at which no decomposition occurred. Let us suppose that we have a beam of acetone molecules, directed at a platinum target that is perfectly plane in the molecular sense and is at a temperature of 1600° C. Under these circumstances the molecules would make only one collision with the surface, and furthermore at this high temperature it seems reasonable to suppose that only a negligibly small fraction of the molecules would be adsorbed for a time which is long compared to the duration of a collision. We are interested in the transfer of energy from the hot platinum surface to the internal degrees of freedom of the molecule, and those molecules that have acquired some internal energy in the collision process will have one or more quanta corresponding to the vibration frequencies in the acetone molecule. If the collisions with the surface are 100 per cent. efficient in the transfer of internal energy, the acetone molecules will leave the surface with a distribution of internal energy corresponding to the temperature of 1600° C.

The heat of activation of acetone may be taken as 68500 cal.,* which is the difference between the average energy of the molecules that can decompose and the average energy of all the molecules. After collision with the platinum surface at 1600° C., some of the acetone molecules will have acquired a very high internal energy content, perhaps much greater than 68500 cal., and will decompose while they are at the surface; others of lower energy content will decompose in their flight from the target to the liquid air-cooled surface, while others may have such a low probability of decomposition that they will be caught on the liquid air surface before decomposing. The fraction of the molecules having energy 68500 cal. or more at 1600° C. may be calculated from the equation†

$$\frac{N}{\Gamma(\frac{1}{2}S)} \left(\frac{Q}{RT} \right)^{\frac{1}{2}S-1} e^{-\frac{Q}{RT}},$$

* Hinshelwood and Hutchinson, 'Proc. Roy. Soc.,' A, vol. 111, p. 245 (1926).

† See Fowler, "Statistical Mechanics," p. 463, Cambridge University Press (1929).

where N is the number of molecules, S is the number of square terms in the energy equation and Q is the heat of activation. This equation can be used in its approximate form even at 1600° because Q/RT is still fairly large. Giving S the value 15, we find that only 0.06 per cent. of the molecules have an energy greater than 68500 cal., and therefore the fraction of molecules capable of decomposition is far too small to detect even when temperature equilibrium with the surface is attained.

The platinum target used in our experiments did not of course have a molecularly plane surface and many of the molecules must have made two or more collisions before leaving it. Some of the molecules doubtless bounced around in minute surface crevices for a long time compared to the duration of a collision, but we may assume that this fraction is negligibly small; unless the probability of transfer of energy from the platinum target to the internal degrees of freedom of the acetone molecule is extremely small, we would observe decomposition if any appreciable fraction of the molecules remained in crevices or were adsorbed at the platinum surface.

In the light of these experiments we may regard the acetone molecules as colliding with the surface and absorbing 0, 1, 2, 3, or more quanta. The probability of decomposition will be zero until the molecule has acquired an amount of energy equal to the heat of the primary decomposition, presumably the breaking of a carbon-carbon bond. Our calculations show that even if the acetone molecules attain the energy distribution corresponding to 1600°C ., only a negligibly small fraction have an energy equal to the heat of activation and this calculation agrees with the experimental result. The experiments with acetone and a platinum target indicate that in continuing the work we must use another organic substance having a lower heat of activation than acetone or use a metal target capable of withstanding higher temperatures than platinum.

We selected dimethyl mercury as a suitable substance to use, having a lower heat of activation than acetone. Its heat of activation has not been measured, but Jones and Werner* reported that it decomposes about 200°C . This is very low decomposition temperature for an organic compound and indicates that if it decomposes unimolecularly it would probably have a heat of activation less than 35000 cal.† Calculations based on this value show that if the dimethyl mercury comes into temperature equilibrium with the platinum target at

* Jones and Werner, 'J. Am. Chem. Soc.,' vol. 40, p. 1257 (1918).

† See Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," p. 159, The Clarendon Press (1929).

1600° C. we should have obtained about 6 per cent. decomposition, whereas in the experiment there was no detectable decomposition.

In view of the experimental results obtained with the platinum target, we decided to repeat the experiments using the much more refractory metals, tantalum and tungsten. Here, unfortunately, we found a new complication which did not occur in the case of platinum. The reaction that takes place on the tungsten or tantalum surface is accompanied by formation of the metal carbide; apparently the specific property of the metal effective in bringing about decomposition of the acetone or dimethyl mercury is the ability to form a metallic carbide, since neither reaction or carbide formation occurs with platinum. We made a search of the literature, but found no definite information about platinum carbide other than a warning in discussing the use of platinum crucibles in analytical procedure to the effect that they must not be heated in a smoky flame, since subsequent heating to higher temperatures causes brittleness and loss of platinum through the formation of platinum carbide. This effect might readily be attributed to either solution of the carbon or solution of hydrogen, both of which might cause brittleness.

The carbides of both tantalum and tungsten are known and have been studied to some extent, and the paper by Friederich and Sittig,* describes these carbides and their melting points, and Andrews gives further information about tungsten carbides.

If the formation of a carbide is a necessary condition for the decomposition of the acetone, the minimum temperature at which decomposition can occur must be higher than the temperature above which the carbide can form. This temperature is not known for tantalum carbide, but Andrews states that tungsten carbide forms above 950° C. The runs with acetone on tungsten at 850° and 940° showed no decomposition, while the run at 1085° showed a trace of decomposition. The minimum temperature of decomposition with tantalum, namely 1400° C., may be taken as the approximate temperature at which the rate of this heterogeneous reaction begins to be appreciable. The slowing up of the rate of decomposition of acetone on tungsten and tantalum targets is attributed to the formation of the carbides which reduces the number of metal atoms on the surface which are active in the decomposition.

We have not been able to find any information regarding the heats of formation of tantalum or tungsten carbides; however, a recent paper by Brantley

* Friederich and Sittig, 'Z. Anorg. Chem.,' vol. 144, p. 174 (1925); Andrews, 'J. Phys. Chem.,' vol. 27, p. 270 (1923).

and Beckman* enables us to calculate that the heat of formation of titanium carbide is over 200,000 cal. per mol. If the heats of formation of tungsten and tantalum carbides have some such high values it is easy to understand that the decomposition of an organic compound at these surfaces is determined by two factors, the first of which is the temperature at which carbide formation occurs at an appreciable rate, and the second is the presence of free metal atoms on the surface of the foil.

Summary.

When acetone or dimethyl mercury in a molecular beam collides with a heated platinum target there is no decomposition up to temperatures of 1600° C. Adsorption on the surface of any appreciable fraction of the molecules for a time very long in comparison with the duration of a collision should cause detectible decomposition; this should also have been observed if any appreciable fraction of the molecules bounced around in minute surface crevices. Since no decomposition occurred, we conclude that adsorption on the surface or the trapping of molecules in cavities does not occur to any appreciable extent when organic vapours at low pressures collide with heated metal targets.

When acetone vapour comes into temperature equilibrium with a target at 1600°, the fraction of the molecules having the energy of activation 65500 cal. is too small to be detected. Dimethyl mercury should have a measurable fraction of activated molecules at this temperature, but since we did not obtain any decomposition we conclude that the transfer of energy from a heated target to the internal degrees of freedom of an organic molecule is not 100 per cent. efficient.

When acetone or dimethyl mercury in a molecular beam collides with a heated tungsten target no decomposition is observed up to a temperature of 1085° C. At this and higher temperatures a surface reaction occurs in which tungsten carbide is formed and carbon monoxide and hydrogen are liberated. This heterogeneous surface reaction only attains an appreciable rate at about 1085° C. Similar results were obtained with a tantalum target except that the reaction did not commence until 1400° C.

* Brantley and Beckman, 'J. Amer. Chem. Soc.,' vol. 52, p. 3956 (1930).

BIOGRAPHY

Harold Theodore Byck, the author of this dissertation, was born December 17, 1902, in New York City. At the age of four he moved to Yonkers, New York, in the public schools of which city he received his primary and secondary school education. He received the degree Bachelor of Science in Chemical Engineering from New York University in 1924. From 1925 to 1928 he served as research chemist with the Bell Telephone Laboratories in New York. During this period he pursued graduate work in physics and chemistry at Columbia University and at the Washington Square College of New York University. He entered the graduate department of the Johns Hopkins University in October, 1928, holding a University Scholarship for the year 1928-1929, and the Grafflin Scholarship for the year 1929-1930.

